



Short communication

Carbon blacks for the extension of the cycle life in flooded lead acid batteries for micro-hybrid applications

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HIGHLIGHTS

- Starter batteries with different carbons were tested under partial state-of-charge conditions.
- Hydrogen reference electrode measurements on the negative electrode complemented electrical data, BET and SEM measurements.
- Homogenously distributed carbon particles can act over the whole negative plate which leads to longer cycle life.

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ABSTRACT

Different carbon blacks were added with quantities in between 0.2% and 2% to the negative active material of flooded lead-acid batteries. By scanning electron microscopy it can be shown that the carbons differ in aggregate structure and particle morphology. In order to test the effectiveness of the carbon blacks, the batteries were subjected to cycle tests with 17.5% depth of discharge. Batteries with carbons in the negative active masses display drastically decreased sulfation of the negative active masses. An extension of the battery lifetime by a factor of 2 could be determined compared to conventional batteries. Furthermore it was noticed that the battery cycle life is influenced by the dispersion properties of the carbon particles into the negative active mass. Particles which are homogenously distributed into the negative active mass are able to act over the whole plate and therefore affect cycle life positively.

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1. Introduction

Batteries for micro-hybrid applications are operated in a partial state of charge (PSoC). In PSoC mode, the battery is exposed to increased cyclic loads. High charging currents and exhaustive discharges lead to an inhomogeneous acid density profile (acid stratification) of sulfuric acid used in the battery. Sulfation, i.e. the precipitation of lead sulfate crystals on the negative electrodes,

leads to premature loss of capacity and early failure of the battery. Carbons are used in a tenth of a percent in the negative active mass, in order to improve the electrical transmission in the active material. Furthermore, the carbons (in particular carbon blacks) are able to adsorb, store, and, if required, release the decomposition products of spreading substances. The carbon blacks protect the electrodes from becoming covered by lead sulfate [1]. Results have been published which show a correlation between the type and quantity of carbons and the improved current draw and cycle life of the battery in PSoC mode [2–5]. Most of the investigations about the effects of carbons in the negative active masses (NAM) were made on batteries with an immobilized electrolyte (e.g. VRLA batteries = valve regulated lead-acid batteries). This research paper reports on carbon blacks (CBs) which are introduced into the

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negative active masses (NAMs) of flooded lead acid batteries (which are cheaper to produce and have no inherent temperature problem due to recombination). In doing so, the focus lies on the examination of the effectiveness of the different CBs in the negative active mass during different electrical tests. Regarding the battery life, different aspects are examined more closely in order to present a summary of the current research status with regard to the flooded lead acid batteries with carbon additives. This research paper underlines what influence the primary particle size of the different carbons has on the battery life, and how it affects the quality of the dispersion of particles in the negative active masses. Using potential measurement versus a H_2 reference electrode, the polarization of the negative electrode (e.g., caused by sulfation) is indicated. By this, we do a complementary investigation to our first results on the importance of ordering in carbons for the performance of flooded batteries [6]. By this, we complement the studies of Pavlov et al. on the influence of carbon on lead-acid batteries [7,8].

2. Experimental

2.1. Characterization of carbon blacks and non-cycled battery electrodes

Different carbon blacks and a lamp black were introduced into the negative active masses of the test-batteries. The carbon blacks and the lamp black were characterized regarding BET-surface, average particle size and particle morphology. In order to evaluate the quality of the dispersion of carbon particles in the negative active masses, non-cycled negative battery electrodes were examined by electron microscopy.

2.1.1. BET surface

The BET surfaces of the carbons were determined with a Micromeritics TriStar 3000. The instrument uses physical adsorption and capillary condensation principles to determine the surface area of the carbons. At -196°C , the material is dosed with nitrogen at a series of precisely controlled pressures. With incremental pressure increases across the range of 0.01 – 0.3 P/P_0 , the BET surface area is determined.

2.1.2. Average particle sizes

The average particle sizes (particle size distribution) were measured with a Honeywell X100 series Microtrac Particle Size Analyzer. With the aid of a surfactant, the carbons are dispersed in water. This suspension is sonicated using a Branson sonic horn for a short period to homogeneously break down soft agglomerates. This suspension is then measured for particle size by laser light diffracting from the sample. This diffracted radiation is projected onto an optical detector array and an algorithm is used to calculate

particle size distribution. The calculation assumes spherical shape and non-transparent particles.

2.1.3. Scanning electron microscopy (SEM)

Images of the pure, powder carbons were taken on a Zeiss Gemini Supra VP40 field emission scanning electron microscope. Photographs were taken at a magnification of $1:50\,000$. The excitation voltage was at 5 kV , the mean working distance 6.3 mm .

For the examination of negative battery electrodes, plate segments of the dry negative electrodes were observed with a Zeiss field emission scanning electron microscope Gemini Supra VP40. The magnification photos of the 1 cm^2 gold-spattered samples (Fig. 1b) were made at $10\,000\times$. The excitation voltage was 5 kV , the mean working distance 6.3 mm .

2.2. Test batteries

$12\text{ V } 59\text{ Ah}$ Enhanced Flooded Batteries (EFBs) were tested. The batteries had a standardized design (LN2 battery boxes, as per EN 50342 [9]). During production of the batteries, 0.2% or 0.3% of CB No. 1, 0.2% of CB No. 2 and 2.0% of the LB were added to the negative active masses of the test-batteries. The reason for the different compositions was to compare the influence of the dispersity of the used carbons. So a parameter that had to be adjusted was the overall surface. In order to do so, lamp black had to be used in much higher concentrations than the other carbons.

Before beginning the battery tests, the open-circuit voltage (OCV), the internal resistance (R_i) (with a Hioki internal resistance measuring device, 3554), as well as the weight were determined (Table 2) in order to rule out processing defects and disparities in the batteries.

2.3. Electrical battery tests

For cyclic aging of the test batteries, three different electrical battery tests were carried out on Digatron BTS-600 test circuits. The tests were carried out in Kustan test basins filled with water at $27 \pm 0/-2^\circ\text{C}$.

2.3.1. Cycle test with 17.5% depth of discharge

During this test, the batteries were cycled after a pre-measurement with the sequence capacity – cold start – capacity – cold start – capacity, as per EN 50342-1 [9], with 17.5% depth of discharge. The following process took place 85 times:

40 min of charging with 20.7 A and a voltage limit of $14.4 (\pm 0.05)\text{ V}$
30 min of discharging with 20.7 A

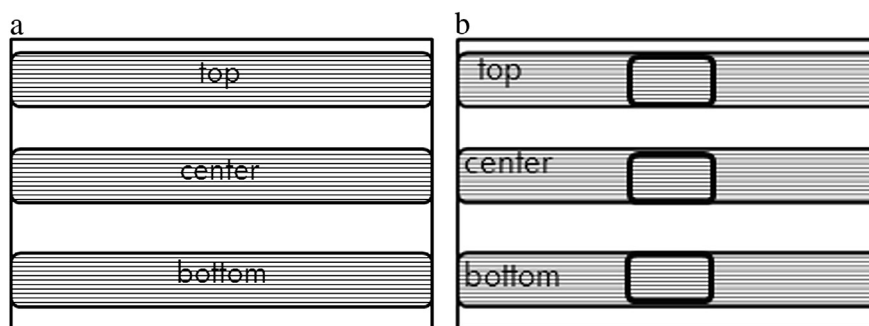


Fig. 1. a. Classification of the negative electrodes in different segments (top, center, bottom) for the wet-chemical analysis. b. Classification of the negative electrodes in different 1 cm^2 segments (top, center, bottom) for the electron microscopic analysis.

After the cycle, an 18-h compensation charge took place with 6 A and 16 V. Afterward, the battery was charged again with 3 A to a final charging voltage of 10.5 V, followed by 23 h of charging with 16 V and 14.8 A. This test process corresponds to one unit (85 cycles = 1 unit) of the 17.5% cycle test. The batteries were cycled until their final charging voltage was under 10 V or until they had passed 18 units (1530 cycles).

2.3.2. Cycle test with 17.5% depth of discharge (intensified)

This test was carried out similarly to the test process described in Ref. [10], but without the mechanical movement.

2.3.3. Potential measurement versus a H_2 reference electrode

The potential of the negative electrodes was measured over the course of 6 units of the 17.5% cycle tests with GaskatelHydroFlex hydrogen reference electrodes (H_2 reference electrodes). In each outer cell of the battery which faces the negative pole, a H_2 reference electrode was inserted. The electrodes were inserted into the electrode chamber by drilling through the plugs located in the middle of the respective cell in the battery cover. These examinations focused on the development of final charging voltages over the course of the cycles.

2.4. Examinations on the negative battery electrodes

Quantitative sulfur analyses of segments from different electrode areas of the cycled battery electrodes were carried out – in particular of the negative electrodes after the electrical tests – in order to determine the degree of aging. Therefore, the negative electrodes were dried in a vacuum drying cabinet (40 °C) after the cycle tests with 17.5% depth of discharge. Subsequently, the dried plates were split into three segments for wet-chemical and electron microscope examinations (Fig. 1a and b). A quantitative determination of the lead sulfate proportion of this segment was performed gravimetrically or by infrared spectroscopy.

2.4.1. Gravimetric determination of lead sulfate of the active masses

Around 5 g active mass of the respective plate segment (Fig. 1a) from the dried negative plates, which were tested with 17.5% depth of discharge in the cycle test, was emitted and finely ground in order to determine the lead sulfate. Barium sulfate was precipitated using barium chloride.

2.4.2. Infrared absorption to determine the lead sulfate of the active masses

Around 5 g active mass of the respective plate segment (Fig. 1a) from the dried negative plates, which were tested with 17.5% depth of discharge in the intensified cycle test, was emitted and finely ground in order to determine the lead sulfate. The $PbSO_4$ content of the respective plate segments (Fig. 1a) was determined via infrared absorption on SO_2 in an induction furnace at 19.5 MHz and maximal 2.2 kW.

3. Results and discussion

In Table 1 the BET-surfaces of the carbon blacks and the lamp black in $[m^2 g^{-1}]$ and the average particle sizes in [nm] are listed. The BET-surfaces of the carbon blacks are very similar; much lower is the one of the lamp black – therefore it was used in a higher percentage (2%, chapter 2.2) in the negative active mass. The average particle sizes of the respective carbons differ more. The lamp black shows the biggest particles, followed by carbon black No. 1 and No. 2 (Table 1).

Table 2 comprises the open-circuit voltages in [V], the internal resistances in [mΩ] and the weight in [kg] of the test batteries. It

Table 1

BET surfaces and average particle sizes of the CBs examined, and the LB.

	BET surface [$m^2 g^{-1}$]	Average particle size [nm]
CB No. 1	243	60
CB No. 2	235	35
LB	29	150

can be seen, that the distributional widths of the values of the respective batteries are similar.

3.1. Characterization of carbon blacks and non-cycled battery electrodes

3.1.1. Particle morphology

Fig. 2 shows the SEM photos of the CBs, types No. 1 and No. 2 as well as the LB used. Differences in size and aggregate structure are visible. The structure of the aggregate made of primary particles is visible at a magnification of 1:50 000. The figures also show that the regularly formed particles are almost circular. The particle size of carbon black type No. 1 is between 25 and 100 nm. The particle size of carbon black type No. 2 is between 20 and 50 nm. The particle size of the LB is between 100 and 200 nm and, just like the CBs No. 1 and 2, has an almost circular shape. The larger size of the LB particles in comparison with the CB particles also explains the lower BET surface of the LB (Table 1).

3.1.2. Particle dispersion in the negative active mass

Fig. 3 shows SEM photos of unformed negative plates with different carbon blacks and the LB. It is evident that the surface of the plate with CB No. 1 (0.2%) is much smoother than the electrode surfaces with CB No. 1 (0.3%) and CB No. 2. The LB particles are distributed very homogeneously on the plate surface – although they are not as homogeneously distributed as the particles of CB No. 1 (0.2%). In particular on the surface of CB No. 2, disordered structures caused by particle agglomerates were visible. The increased formation of agglomerates can be explained by the small particle size (Table 1) – the smaller the particles, the higher the tendency to agglomerate to particle clusters. If a higher number of particles is used, (such as for CB No. 1 0.3%), this also results in an increased formation of agglomerates (Fig. 3).

Based on these observations made by scanning electron microscopy, it is proposed that electrochemical processes (e.g. diffusion, reactant conversion) run more uniform, if the carbon particles are homogeneously distributed in the active material. Conversely, this means that an inhomogeneous distribution of carbons in the negative active mass leads to changed transport processes.

3.2. Evaluations of electrical tests

This section explains the effects of the material properties of the different carbon-containing NAMs described in Section 3.1 on the cycle life of the batteries. Furthermore, the aging-related polarization (caused by sulfation) of the negative electrode using measurements with H_2 reference electrodes is documented.

Table 2

Open-circuit voltage [V], internal resistance R_i [mΩ] and weight [kg] of the test batteries.

	OCV [V]	R_i [mΩ]	Weight [kg]
Batteries (CB No. 1, 0.2 %)	12.69–12.71	3.50–3.60	18.4–18.5
Batteries (CB No. 1, 0.3 %)	12.69–12.72	3.50–3.60	18.3–18.4
Batteries (CB No. 2)	12.69–12.70	3.45–3.60	18.4
Batteries (LB)	12.71–12.74	3.50–3.60	18.3

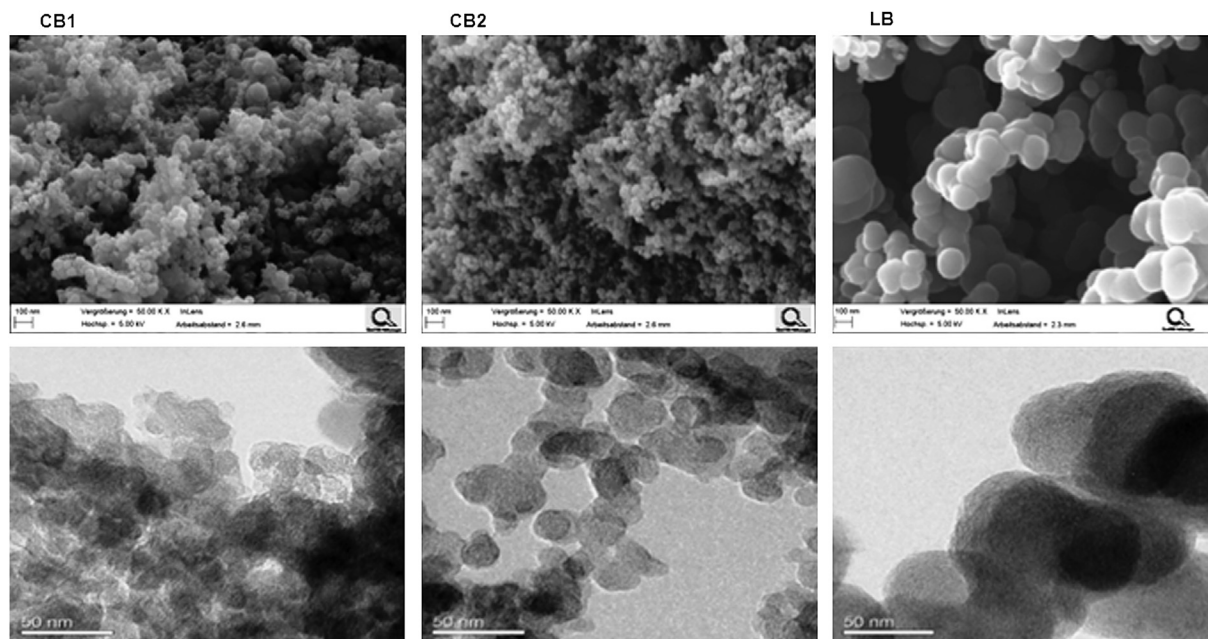


Fig. 2. SEM (top) and TEM (bottom) pictures of the different carbon blacks.

3.2.1. Cycle tests with 17.5% depth of discharge

The batteries with the LB and CB No. 1 show no significant difference in the intensified 17.5% cycle test (B) at 500 to 540 cycles, the battery with CB No. 2 only reached 435 cycles (Fig. 4).

A reference battery without carbon in the negative active mass failed after only 250 cycles (Fig. 4). All test batteries with carbon in the negative active mass showed similar distribution of PbSO_4 on the negative plate after the cycles (Table 3). The reference battery

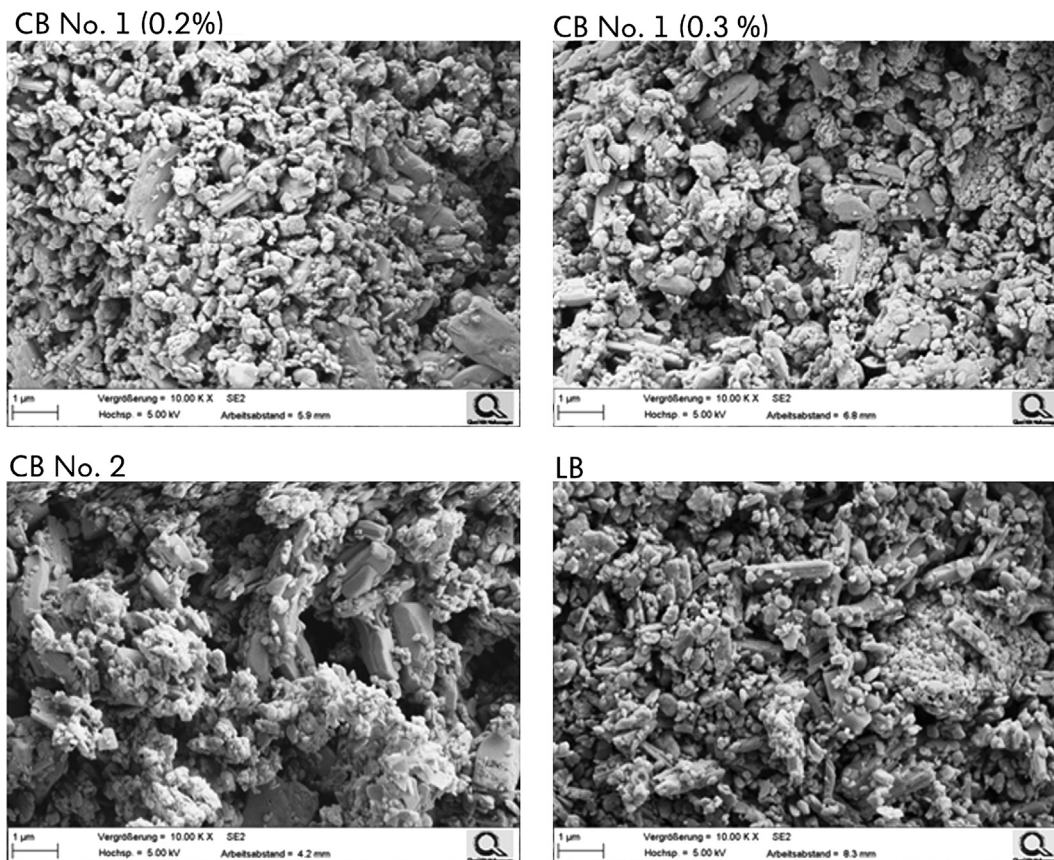


Fig. 3. 10,000× magnification of the negative uniform battery electrodes with CB No. 1 (0.2%), CB No. 1 (0.3 %), CB No. 2, and LB (from left).

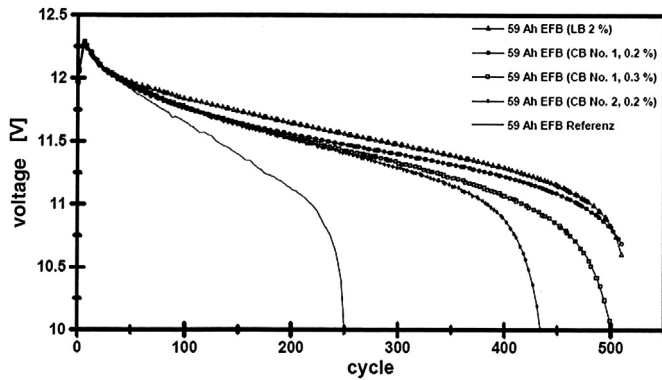


Fig. 4. Course of the cutoff voltages in the intensified 17.5% cycle test.

without any carbon in the negative active mass showed significantly more sulfation, especially in the central section of the electrode (Table 3). The fact that the battery with this carbon type (CB No. 2) performs comparatively bad in the intensified cycle test with 17.5% depth of discharge is possibly caused by the particles being poorly dispersed on the plate and the units being considerably agglomerated (Fig. 3). The particle agglomerates interact with each other, which leads to interference of the ion migration. This means the local high current densities lead to a suspension of the charge reaction, as the supply of lead ions is limited. The less contact sides the particles have between each other, the worse is the charge transport and the electrical conductivity.

In the cycle test with 17.5% depth of discharge (A), the battery with LB passed most cycles without the voltage dropping significantly (Fig. 5). The negative plates have a low level of sulfation after the cycles (Table 4). Similar behavior was observed in the batteries with CB No. 1 (0.2%) and, against expectation, also CB No. 2 (Fig. 5). These batteries also showed minimal sulfation of the negative plates. Whether the equalization charges in the 17.5% cycle test (A) offset the negatively affected properties of CB No. 2 in the intensified 17.5% cycle test, or whether other factors contributed to the favorable potential course of this battery (Fig. 5), is currently under investigation. The strongest voltage dip was seen in the battery with CB No. 1 (0.3%) in the NAM (Fig. 5). The battery with this CB is the only one which reached the voltage switch off criterion before the end of the test. The other batteries were in a voltage range of over 11.5 V after more than 1500 cycles without significant differences. Obviously the quantities of CB used depending on the unit structure also played a role. The fact that the battery with CB No. 1 (0.3%) failed in the 17.5% cycle test (A) can be explained by the following: the current densities not only prevailed locally, but across the whole plate. Fig. 3 supports this statement: on the surface of the negative plate of the battery with CB No. 1 (0.3%) there are – in contrast to the battery with 0.2% CB No. 1 – more

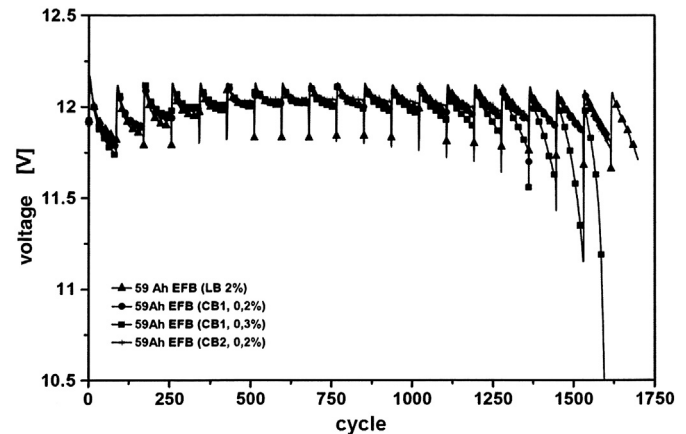


Fig. 5. Course of the end of discharge voltages in the cycling test with 17.5% depth of discharge (A).

agglomerates. Furthermore, after cycling the battery with the CB No. 1 (0.3%) shows strong sulfation in the central and lower area of the negative electrode (Table 4). However, it is remarkable that, although LB was present in quantities ten times higher in the NAM, a considerably longer service life was achieved. This is due to the fact that the LB-particles do not agglomerate so strongly and thus don't cause locally high current densities; instead they are statistically more uniform and spread over the whole electrode, meaning that they are effective across the whole active mass (Fig. 3).

The potential measurements versus a H_2 reference electrode reflect the behavior of the test batteries in the 17.5% cycle test (A). Fig. 6 shows the charging potentials of the negative electrode at the end of the each microcycle, measured against H_2 reference electrodes during the first and the last unit of the 17.5% cycle test (A). The changes of these charging potentials are the result of polarization of the negative electrodes caused by aging. The development of these charging potentials with increasing number of cycles is therefore a measure of the reaction inhibitions. These inhibitions occur, for example, due to an increasing sulfation on the negative electrodes [11]. Comparing the units, the first striking fact is that no significant changes to the starting value can be observed at the beginning of the two test units. With CB No. 1 (0.3%), a fast descent of the potentials throughout is noticeable, while the remaining carbons demonstrate primarily flat curves. In contrast to the other test batteries, this battery (CB No. 1, 0.3%) shows significantly sulfated plates after the cycles, particularly in the central area (Table 4). The potential course of the battery with CB No. 2 is almost constant between -0.5 V and -0.6 V, i.e., the polarization is lowest with this carbon in all units; the plates show a very small level of sulfation (Table 4). This corresponds to the behavior of the battery with CB No. 2 which was observed in the 17.5% cycle test (A).

Table 3

Lead sulfate content [%] of the negative active masses after cycles with 17.5% depth of discharge (determination of the $PbSO_4$ content using infrared adsorption).

	PbSO ₄ -content in the NAM [%]		
	Top	Center	Bottom
59 Ah EFB with CB/LB			
CB1 (0.2 %)	3.4	5.02	75.36
CB1 (0.3 %)	3.33	4.18	67.31
CB2	2.85	6.45	79.21
LB	2.06	8.25	77.88
Reference (without any C in the NAM)	2.3	11.8	58.7

Table 4

Lead sulfate content [%] of the negative active masses after cycles with 17.5% depth of discharge (determination of the $PbSO_4$ content using gravimetry).

	PbSO ₄ -content in the NAM [%]		
	Top	Center	Bottom
59 Ah EFB with CB/LB			
CB1 (0.2 %)	2.4	6.5	63.7
CB1 (0.3 %)	3.5	26.8	82.9
CB2 (0.2 %)	3.6	7.4	77.8
LB (2 %)	2.1	6.8	66.8

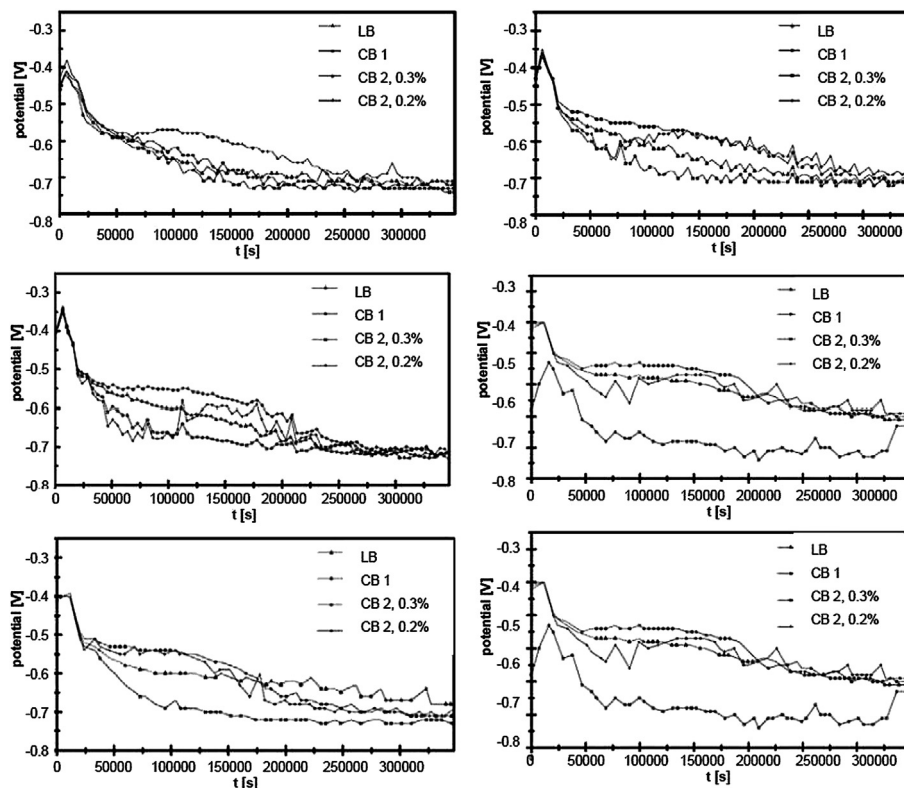


Fig. 6. Measurements with hydrogen reference electrodes on the negative electrode of the units 1–6 (from the top left) of the 17.5% cycle test (A).

To the best of our knowledge, such curves have not been described in the literature before. It is to conclude that, during the cyclic operation or during the equalization charging, permanent changes occur which obviously do not correspond to the known aging mechanisms (such as sulfation) of the negative electrodes. This means that sulfation in the potential curve would be evident right at the start of the subsequent unit (such as the battery with CB No. 1, 0.3%). For the permanent changes, which cause the altered potentials, a redistribution of the carbon particles in the negative active mass is possible, as described for example in Fig. 7. Due to the fact that the density of lead sulfate is lower than the density of lead, the sulfation of the negative electrodes leads to an expansion of the negative active material. The carbon particles are subsequently pushed out of the active material during the cycles and finally swamped out of the electrode by the electrolyte or gassing. This finding was confirmed by opening the batteries after cycling. The electrolyte was – instead of having its usual light gray color – dark

black. The migration of the carbon particle is problematic because the carbon is no longer effective in the interior of the electrodes, i.e., in the interior of the negative plate in an aged battery, the reaction of Pb^{2+} to Pb is no longer facilitated.

4. Conclusions

The results of the material characterization with regard to the better life in tests with 17.5% DoD allow the following conclusions:

- (1) Batteries with carbon blacks in the negative active mass display lower plate sulfation and therefore a significantly longer battery life in cycle tests with 17.5% depth of discharge, compared with batteries without carbons in the negative active mass.
- (2) The carbon particles exhibited different nm-range particle sizes. It turned out that the smaller the particles, the higher the tendency to create agglomerates in the electrodes. This effect is likely related to the paste mixing process which leads to less dispersed carbons when small particle size carbons are used. During scanning electron microscopic observation of unformed plates into which the carbons were introduced, it was found that the particle size and the particle quantity used are relevant. The smaller the particles, the stronger the agglomeration, meaning that the particles are also distributed more poorly in the active material. The same effect occurs when using large quantities of carbon materials. With regard to the battery life, there were clear indications that inhomogeneously dispersed particles in the plate lead to a shortened cycle life of the battery (in particular during the intensified 17.5% cycle test). Using potential measurement versus a H_2 reference electrode, this observation could also be confirmed in the 17.5% cycle test (A), see Section 4.

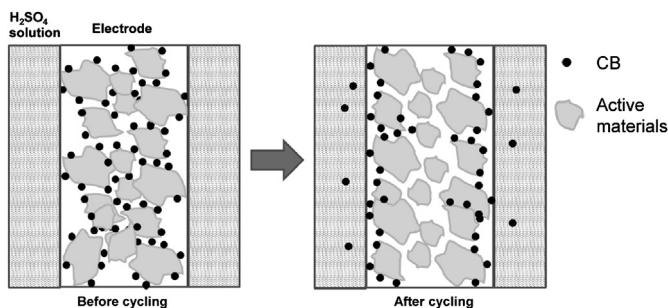


Fig. 7. Carbon particle distribution in the negative active material before and after cycling.

- (3) Potential measurement versus a H₂ reference electrode confirmed the observations which were made during the 17.5% cycle test (A). These measurements showed that the aging process of batteries is multicausal. So a new observation found was that the course of the end-of-discharge voltages beyond the cycle test units was much flatter, which can only be explained by irreversible changes to the electrodes. An explanation for this is the redistribution or separation of the carbon particles from the active material, with the consequence that the carbon particles can no longer exert their positive effect within the material.
- (4) The evaluation of the potentials of the negative electrode indicates that the mechanisms of actions of carbons are more complex in flooded batteries than in valve-regulated ones (cf. that Micka et al. found out that it is mainly the geometry that determines the performance of the negative electrode in partial state-of-charge cycling [12]). In particular, chemical aspects seem to play a major role in flooded batteries.

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